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## Recent Work

### Title

Impacts of Mixed-Wettability on Brine Drainage and Supercritical CO<sub>2</sub> Storage Efficiency in a 2.5-D Heterogeneous Micromodel

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1 Impacts of Mixed-Wettability on Brine Drainage and  
2 Supercritical CO<sub>2</sub> Storage Efficiency in a 2.5-D  
3 Heterogeneous Micromodel

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24 Key points

- 25 1. We created two mixed-wet systems with varying water- and  
26 intermediate-wet patches in a 2.5-D heterogeneous micromodel;
- 27 2. The uniformly distributed intermediate-wet patches yield  
28 bridging flow topology and highest storage efficiency after  
29 drainage;
- 30 3. The heterogeneously distributed intermediate-wet patches  
31 enhance channelized CO<sub>2</sub> flow and hinder storage efficiency after  
32 drainage.

**Abstract:** Geological carbon storage (GCS) involves unstable drainage processes, the formation of patterns in a morphologically unstable interface between two fluids in a porous medium during drainage. The unstable drainage processes affect CO<sub>2</sub> storage efficiency and plume distribution, and can be greatly complicated by the mixed-wet nature of rock surfaces common in hydrocarbon reservoirs where supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is used in enhanced oil recovery. We performed scCO<sub>2</sub> injection (brine drainage) experiments at 8.5 MPa and 45 °C in heterogeneous micromodels, two mixed-wet with varying water- and intermediate-wet patches, and one water-wet. The flow regime changes from capillary fingering through crossover to viscous fingering in the micromodels of same pore geometry but different wetting surfaces at displacement rates with  $\log Ca$  (capillary number) increasing from  $-8.1$  to  $-4.4$ . While the mixed-wet micromodel with uniformly distributed intermediate-wet patches yields  $\sim 0.15$  scCO<sub>2</sub> saturation increase at both capillary fingering and crossover flow regimes ( $-8.1 \leq \log Ca \leq -6.1$ ), the one heterogeneous wetting to scCO<sub>2</sub> results in  $\sim 0.09$  saturation increase only at the crossover flow regime ( $-7.1 \leq \log Ca \leq -6.1$ ). The interconnected flow paths in the former are quantified and compared to the channelized scCO<sub>2</sub> flow through intermediate-wet patches in the latter by topological analysis. At  $\log Ca > -6.1$  (near well), the effects of wettability and pore geometry are suppressed by strong viscous force. Both scCO<sub>2</sub> saturation and

56 distribution suggest the importance of wettability on CO<sub>2</sub> storage  
57 efficiency and plume shape in reservoirs, and capillary leakage through  
58 caprock at GCS conditions.  
59

## 60 **1. Introduction**

61 Geological carbon storage (GCS) in subsurface reservoirs has  
62 significant capacity for reducing greenhouse gas emissions into the  
63 atmosphere (IPCC, 2005). Key questions include (1) the storage  
64 efficiency of a geological formation, which is the fraction of the total  
65 pore space used by GCS (Bachu et al., 2007; Goodman et al., 2011),  
66 and (2) the spread of a CO<sub>2</sub> plume, which needs to be monitored and  
67 controlled to ensure safe and permanent storage (Nordbotten et al.,  
68 2005; Juanes et al., 2010; Doughty et al., 2010; MacMinn et al., 2010,  
69 2011). Both questions are closely related to the migration of the CO<sub>2</sub>  
70 plume during injection, with formation brine (the wetting fluid)  
71 displaced by supercritical CO<sub>2</sub> (scCO<sub>2</sub>, the non-wetting fluid). One of the  
72 major reasons for inefficient CO<sub>2</sub> storage in the subsurface is unstable  
73 displacement characterized by fingering flow due to the low viscosity  
74 of scCO<sub>2</sub> relative to formation brine (typical ratio ~1:20) (Zhang et al.,  
75 2011a,b; Wang et al., 2012; Berg & Ott, 2012). The unstable  
76 displacement and fingering flow of scCO<sub>2</sub> will also increase leakage  
77 potential through caprock (Tsang et al., 2008), non-equilibrium CO<sub>2</sub>  
78 dissolution (Chang et al., 2013, 2014, 2016, 2017, 2019a,b), and  
79 mineral trapping (Sanchez-Vila et al., 2007; Huq et al., 2015) after  
80 injection ceases.

81 Unstable displacement can be further complicated by the solid  
82 surface wettability. While deep saline aquifers for GCS typically show

83 water-wet behavior, depleted hydrocarbon reservoirs, where  $\text{scCO}_2$  has  
84 been used for enhanced oil recovery and carbon sequestration, can  
85 exhibit intermediate-wet or mixed-wet rock surfaces (Salathiel, 1973;  
86 Anderson, 1987a,b). It also has been observed the  $\text{scCO}_2$ -induced  
87 wettability changes from water-wet to intermediate-wet on rock  
88 surface (Yang et al., 2008; Broseta et al., 2012; Jung & Wan, 2012;  
89 Seyyedi et al., 2015), in glass micromodels (Kim et al., 2015), and in  
90 glass beads and sand pack columns (Tokunaga et al., 2013; Wang &  
91 Tokunaga, 2015; Lv et al., 2017). These changes occur in local patches  
92 where water films are thin and ionic strengths are high, yielding a  
93 mixed-wet system (Kovscek et al., 1993; Jung & Wan, 2012). Many  
94 studies have investigated the effects of uniform solid surface  
95 wettability (from water-wet to intermediate-wet) on displacement  
96 characteristics, non-wetting phase distribution and capillary trapping at  
97 the reservoir scale (Al-Khdheewi et al., 2017), the core scale (e.g.,  
98 Anderson, 1987a,b; Morrow, 1990; Levine et al., 2014), and the pore  
99 scale (Cottin et al., 2011; Zhao et al., 2016; Hu et al., 2017a,b). At the  
100 pore scale, flow dynamics of individual oil ganglions have been  
101 recently imaged in a single pore/pore throat with mixed-wet solid  
102 surfaces by a synchrotron-based X-ray computed tomography (Rücker  
103 et al., 2019). The unstable displacement and  $\text{scCO}_2$  saturation in  
104 mixed-wet pore networks remain poorly understood, may greatly



105 complicate the modeling predictions (Celia et al., 2015), and need  
106 systematic study.

107 Two-phase flow and displacement have been widely investigated  
108 using two-dimensional (2-D) micromodels monitored with high-  
109 resolution optical imaging systems. “2-D” here indicates the pore  
110 network has varying pore sizes in the horizontal plane, but has a  
111 uniform depth in the vertical dimension. The classic capillary number ( $Ca$ ), in its original form:  $Ca = \mu \times \bar{u} / \sigma$ , was used to interpret the fingering  
112 geometry in a Hele-Shaw cell by Saffman & Taylor (1958). In this  
113 definition,  $\mu$  is the viscosity of the resident fluid,  $\bar{u}$  is the average Darcy  
114 velocity of the injected fluid, and  $\sigma$  is the interfacial tension between  
115 the injected and resident fluid. Given negligible influences of  
116 gravitational forces in thin micromodels, the classic  $Ca$ , along with the  
117 viscosity ratio ( $M$ ) defined as the ratio of viscosities of the displacing  
118 (non-wetting) and displaced (wetting) fluids, were used to characterize  
119 the pore-scale regimes of stable displacement, capillary fingering,  
120 viscosity fingering, and their crossover. Different types of micromodels  
121 have been developed to investigate the two-phase displacement  
122 fundamentals that include (1) homogeneous pore networks composed  
123 with regular cubic, cylindrical, elliptical and hexagonal posts (Xu et al.,  
124 1998; Ferer et al., 2004; Cottin et al., 2010; Zhang et al., 2011a,b;  
125 Wang et al., 2012; Armstrong & Berg, 2013; Chang et al., 2019a,b), (2)  
126 heterogeneous pore networks with irregular cylindrical posts (Zarikos

et al., 2018), (3) statistically generated pore networks with or without spatial correlation of pore sizes (Tsakiroglou & Avraam, 2002), and (4) heterogeneous pore networks fabricated from a section micrograph of natural consolidated sandstone (Zuo et al., 2013) and transparent cells packed with unconsolidated, single-layered glass beads (Moebius & Or, 2014). Some other studies have reported better description of the pore-scale viscous and capillary forces using modified  $Ca$  that considers the length scales corresponding to the size of non-wetting phase clusters (Hilfer & Øren, 1996; Armstrong et al., 2014; Chang et al., 2019a). Common to all of the above studies is the use of 2-D geometry of pore network that has a constant pore/pore throat depth. Lacking ability to continuously record in-situ and dynamic interfacial curvature, measured pore widths and depths were used to calculate the capillary pressure using Young-Laplace equation. The dependence of this relation on the sum of the inverse of two orthogonal radii of curvatures shows that constant-depth micromodels effectively fix one of the principal radii, thus limiting the range of capillary pressures achievable through variation of pore widths. The pioneering work from Wan et al. (1996) improved the glass micromodel design and fabrication to provide the necessary contrast of depths (thus capillarity) between matrix pores and fracture apertures. In recent years, more 2.5-D micromodels have been used to better mimic real 3-D porous media and investigate multiphase flow (Park et al., 2015; Yun

et al., 2017; Xu et al., 2017a,b). To our best knowledge, there are few studies on unstable drainage processes in micromodels having 2.5-D pore geometry heterogeneity, especially for GCS applications, and none that have examined impacts of mixed wetting.

In this study, we (1) create mixed-wet systems by heterogeneously applying octadecyltrichlorosilane (OTS, 0.2% by vol. in hexane) flow to modify surface wettability of a 2.5-D micromodel in two ways, (2) investigate the scCO<sub>2</sub> displacement characteristics and compare the steady-state scCO<sub>2</sub> saturations for water-wet and the two types of mixed-wet micromodels; and (3) quantify the scCO<sub>2</sub> flow characteristics at both pore- and pore-network scale through a topological analysis. We conducted a series of experiments by injecting scCO<sub>2</sub> into an initially brine-saturated micromodel at displacement rates resulting in  $\log Ca$  (logarithm of the capillary number) ranging from  $-8.1$  to  $-4.4$ , allowing investigation of capillary through viscous fingering (at constant  $M = 0.038$ ). For simplicity and ease of comparisons with other studies, the first form of the capillary number  $Ca$  used in this presentation does not include a contact angle term. Later, the capillary number  $Ca^i$  containing the cosine of the effective contact angle will be introduced for comparison. Images of scCO<sub>2</sub> and water distribution were obtained at appropriate junctures to provide direct observations on the pore-scale displacement characteristics and

173 scCO<sub>2</sub> saturation in these pore networks having heterogeneity in both  
174 2.5-D pore geometry and surface wettability.

## 175 **2. Materials and methods**

### 176 **2.1 2.5-D micromodel**

177 Figure 1(a) shows the 2.5-D pore network contained in a 20 mm  
178 ×10 mm rectangle, with a porosity of 0.43 and pore volume of 3.44 μL.  
179 The pore network, with pore space shown in white and solid posts in  
180 black, was extracted from micro-CT images of sand pack of irregular  
181 shaped sand grains, then etched on two symmetrical silica wafers with  
182 hydrofluoric acid and then fused together (Micronit Microfluidics BV,  
183 Netherlands). The different depths of pores and pore throats were  
184 created through etching two mirror image networks, both to 20 μm  
185 depths, but with one face having locations left unetched. Thus, 40 μm  
186 depth pores are created at locations where both faces were etched to  
187 20 μm, while 20 μm deep throats were created at locations where only  
188 one face was etched. Direct aligned bonding of the two plates was then  
189 performed by creating a prebond between the two wafers, which was  
190 then annealed at high temperature. Given the strong bonding, the  
191 micromodel can be operated under the pressure difference (inside  
192 relative to outside) up to 10 MPa, without applying any confining  
193 pressure as has been required in other high-pressure micromodels  
194 (Zhang et al., 2011a; Chang et al., 2016). Figure 1(b) shows the 2-D  
195 pore-size distribution (without taking into account the depth of the

micromodel) characterized by a local thickness plugin in ImageJ software (Hildebrand and Rüesgsegger, 1996; Rasband, 1997-2019). The average pore and pore-throat size are 190 and 48  $\mu\text{m}$ , respectively, while the average post size is 290  $\mu\text{m}$ .

The pore network also contains a capillary barrier transverse to the flow direction (marked by the yellow lines in Figure 1(a) and 1(c)), composed by a line of tight pore throats 20  $\mu\text{m}$  deep. Figure 1(d) depicts the capillary entry pressure along the capillary barrier, calculated from the pore/pore throat size and depth as follows:

$$p_b = \frac{\sigma \cos \theta (r_1 + r_2)}{r_1 r_2} \quad \text{Eq. (1)}$$

Fluid properties		Displacement rate		
Pressure	8.5 MPa	Q ( $\mu\text{L}/\text{min}$ )	$\bar{u}$ (m/d)	$\log Ca$
Temperature	45 °C	0.1	0.8	-8.1
Viscosity scCO <sub>2</sub> /water (mPa·s)	0.023/0.597	0.5	4.2	-7.4
Viscosity Hexane/EG (mPa·s)	0.30/16.90	1.0	8.4	-7.1
Interfacial tension (mN/m)	28.5	2.0	16.7	-6.8
Micromodel properties		5.0	41.9	-6.4
Dimension (cm <sup>2</sup> )	2.0 × 1.0	10	83.7	-6.1
Pore volume ( $\mu\text{L}$ )	3.44	20	167.4	-5.8
Porosity	0.43	50	418.6	-5.4
Pore/throat depth ( $\mu\text{m}$ )	40/20	100	837.2	-5.1
Pore/throat/post diameter ( $\mu\text{m}$ )	190/48/290	200	1674.4	-4.8
scCO <sub>2</sub> /water contact angle	27°	500	4186.0	-4.4

where  $\sigma = 28.5$  mN/m (Chiquet et al., 2007),  $\theta$  is measured as 27° for scCO<sub>2</sub> and brine (see Section 3.1 for more details),  $r_1$  is the local pore radius quantified from Figure 1b and  $r_2$  is the half pore depth. Although

40  $\mu\text{m}$  deep pores are distributed throughout the micromodel, as shown in Figure 1(c) and 1(d), there are only eight of these pores along A-A' (marked by the red arrows), with the others being 20  $\mu\text{m}$  deep. These eight locations will be referred to as "slots" because they constitute pores with low capillary entry pressures. The impacts of this unique characteristic on  $\text{scCO}_2$  invasion patterns for water-wet and mixed-wet conditions will be presented in Section 3. Table 1 lists more details on the pore network.

Table 1. Summary of experimental conditions, fluid and micromodel properties, volumetric flow rates, and corresponding Darcy velocities and capillary numbers

**Figure 1.** (a) Pore characteristics of the 2.5-D micromodel used in this study, with solid posts shown in black, large pores 40  $\mu\text{m}$  deep shown in white and tight pore throats 20  $\mu\text{m}$  deep in red. (b) The pore size distribution quantified by the Local Thickness plugin in ImageJ

software. (c) The sub-image magnified from the red box in (a) that shows the transverse capillary barrier in the pore network. (d) The capillary entry pressure of pores and pore throats for scCO<sub>2</sub>-water displacement with water-wet solid surface ( $\theta = 27^\circ$ ) along the yellow dotted line A-A' shown in (a) and (c). S1 to S8 (marked by the red arrows in (c)) are the open slots in the capillary barrier with reduced capillary entry pressure that may provide potential flow paths for CO<sub>2</sub> invasion. The blue box in (a) and (c) bounds the local pore domain that correlates to the narrow intermediate-wet choke point in Figure 3(c) and constrained scCO<sub>2</sub> flow in Figure 4(b). The blue arrow indicates the scCO<sub>2</sub> flow direction during the displacement experiments.

## **2.2 Mixed-wet treatment**

Contacting the water-wet glass surface with octadecyltrichlorosilane (OTS) strongly impacts the wettability, changing it towards non-water wetting. The coating solution was prepared by diluting octadecyltrichlorosilane (Cole-Parmer, IL) with hexane (ACS grade, Cole-Parmer, IL) in 4.0%, 0.4% and 0.2% volumetric fractions. Before modifying wettability of the glass micromodel, treatment tests on glass microscope slides were conducted following the sequential steps of (1) acid cleaning, (2) coating in OTS/hexane solution, (3) rinsing in hexane to remove excess OTS, and (4) drying in oven at 100 °C. Contact angle measurements of a water droplet on the microscope slides show

values change from  $0^\circ$  to  $\sim 75^\circ$  after treatment by the three concentrated solutions. The contact angle remains constant for over 2 years, indicating the long-term effectiveness of the method (Figure S1 of the supporting information (SI)). The lowest concentrated (0.2% v/v) OTS solution was selected for micromodel treatment to minimize potential effects from the excess OTS. A similar OTS/hexane solution has also been used for changing glass surface wettability in a previous study (Goodwin et al., 2016).

To create a mixed-wet system in the micromodel, we used the OTS/hexane solution as the invading fluid into an ethylene glycol (EG, wetting phase) saturated micromodel. During the treatment, we were able to easily observe the two-phase interface and wettability-altered pore domain because we colored the EG with sulphorhodamine B and collected images of dyed EG distribution under UV light. A low dye concentration (0.23 g/L) was used to minimize its potential effect on fluid viscosity, while allowing sufficient optical detection for phase discernment. The viscosities of the coating solution and dyed EG were assumed equal to that of hexane (0.3 mPa·s) and EG (16.9 mPa·s) due to the low OTS and dye concentration, while the interfacial tension (IFT) between hexane and dyed EG at ambient conditions was measured as 20.5 mN/m through a high-precision tensiometer (Kruss, Germany). Note the close viscosity ratio and IFT between hexane-EG under ambient conditions and scCO<sub>2</sub>-water system under designated



278 experimental conditions (at 8.5 MPa and 45°C,  $\mu_{CO_2}=0.02$  mPa·s,  
279  $\mu_{brine}=0.6$  mPa·s, IFT: 28.5 mN/m). With these similarities, the mixed-  
280 wet pattern induced by hexane-based coating solution and EG was  
281 expected to be similar to that induced by scCO<sub>2</sub>-brine at GCS  
282 conditions. This was experimentally validated and is presented in  
283 Sections 3.2 and 3.3.

284 During treatment, the micromodel was first acetone cleaned, air  
285 dried and then saturated with dyed EG. The surface coating OTS  
286 solution was then injected at constant flow rates using a syringe pump  
287 (Harvard Apparatus, Holliston, MA). Over 3 and 300 pore volumes (PVs)  
288 of coating solution were injected into the micromodel at 3  $\mu$ L/hour (  
289  $\log Ca=-7.2$ ) and 6000  $\mu$ L/hour ( $\log Ca=-3.9$ ), respectively, until the  
290 two-phase distribution in the pore network remained constant with  
291 time. After ten displacement experiments with varying injection rates  
292 between them using hexane and EG, we selected the minimum and  
293 maximum rate injections, which represent potential mixed-wet  
294 patterns induced by capillary fingering (minimum rate injection) and  
295 viscous fingering (maximum rate injection). Other mixed-wet patterns  
296 may vary between them, but we think these two are the boundary  
297 cases that worth of detailed investigation. The coating solution  
298 injection ceased after soaked for over 20 min in the pore network,  
299 followed by 100 PVs of hexane injection to remove excess OTS from  
300 the pore network. Finally, the micromodel was air-dried and cured in

the oven at 100° for 1 hour, similar to the treatment on microscope glass slides. Fluorescent images were acquired to characterize the mixed-wet patterns using a Sony FDR-AX100 camcorder with a spatial resolution of 4.5  $\mu\text{m}/\text{pixel}$ .

### **2.3 Experimental setup and procedures**

A high-pressure, elevated-temperature setup (Figure 2) was built based on Hu et al. (2017b) for  $\text{scCO}_2$  displacement experiments in the water-wet and two mixed-wet micromodels. To establish the initially brine-saturated conditions, low pressure gaseous  $\text{CO}_2$  was first injected into the micromodel to displace air from the micromodel and tubing. It should be noted that, to avoid corrosion, our “brine” was a low salinity solution (0.01 M NaCl). This brine was then injected from the back-pressure pump to displace and dissolve the gaseous  $\text{CO}_2$  through  $\text{E} \rightarrow \text{D} \rightarrow \text{C} \rightarrow \text{B} \rightarrow \text{F} \rightarrow \text{H}$ . During these steps, the micromodel system was kept at atmospheric pressure. Similar low salinity brine was also used by Hu et al. (2017b), with an aim to minimize any wettability changes induced by salinity and ionic composition (Fathi et al., 2010, Karadimitriou et al., 2019).

The  $\text{scCO}_2$  pump was initially filled with wet  $\text{CO}_2$  at approximately 5.87 MPa from a source tank (99.99% purity, Airgas) while Valve A connecting  $\text{scCO}_2$  pump to the micromodel was closed. The  $\text{scCO}_2$  pump was then pressurized up to 8.5 MPa. The pressure in the micromodel and pipeline  $\text{E} \rightarrow \text{D} \rightarrow \text{C} \rightarrow \text{B} \rightarrow \text{F} \rightarrow \text{G}$  was gradually increased to

324 8.5 MPa using the back-pressure pump filled with brine, while keeping  
325 valve G connecting to the brine pump closed. All fluids were then  
326 allowed to equilibrate at 45 °C for over 12 hours. The pressure and  
327 temperature represent reservoir conditions at depths of about 1.0 km.

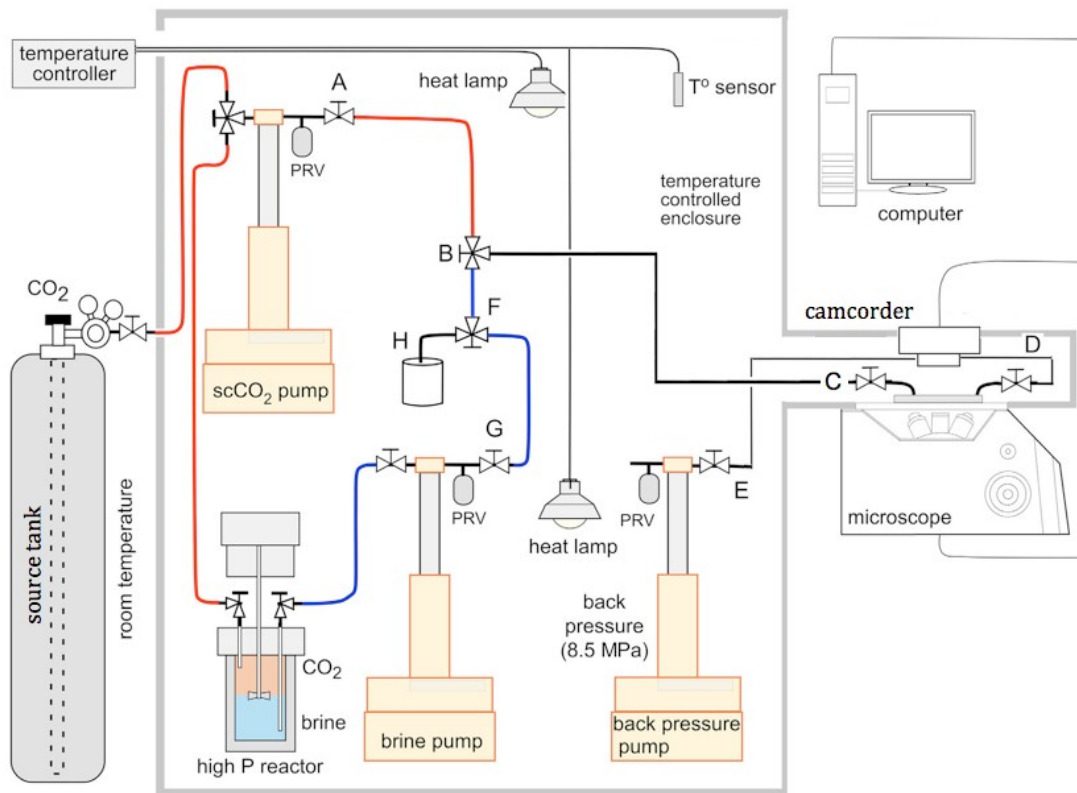
328 To prepare the mutually saturated brine and scCO<sub>2</sub>, 200 mL brine  
329 was first injected into the high-pressure reactor (see Figure 2), and  
330 then pressurized up to 8.5 MPa by CO<sub>2</sub> injection. The reactor containing  
331 scCO<sub>2</sub> and brine was heated up to 45 °C and stirred for 24 hours. The  
332 scCO<sub>2</sub>-saturated brine was then transferred to the brine pump. Over  
333 100 PVs of scCO<sub>2</sub>-saturated brine was then injected to completely  
334 saturate the micromodel and the pipelines through G→F→B→C→D→E.  
335 Displaced fluid was collected in the back-pressure pump, and the  
336 micromodel and fluid delivery pipelines were kept constant at 8.5 MPa  
337 and 45 °C.

338 After the above steps were completed, pre-wetted scCO<sub>2</sub> in the  
339 scCO<sub>2</sub> pump was injected into the micromodel at a specific constant  
340 flow rate. Displaced brine was collected in the back-pressure pump,  
341 which was maintained at a constant withdrawal rate matched to that of  
342 the scCO<sub>2</sub> injection. In this way, we obtained good experimental  
343 reproducibility under the exactly same experimental conditions (see  
344 more details in Figure S2 of SI). When the quasi-steady state was  
345 reached, i.e., scCO<sub>2</sub> distribution and saturation remained constant with  
346 time, scCO<sub>2</sub> injection was stopped. The micromodel was then flooded

347 with scCO<sub>2</sub>-saturated brine until no scCO<sub>2</sub> was observed, to prepare the  
348 micromodel for the next experiment, conducted at a different scCO<sub>2</sub>  
349 injection rate. This sequence was repeated for a wide range of flow  
350 rates. To avoid any contamination effects on the pore surface  
351 wettability during the displacement tests, no dye was employed in  
352 either the scCO<sub>2</sub> or brine. Table 1 lists the imposed volumetric injection  
353 rates in the three micromodels. These rates correspond to a range of  
354 Darcy velocities from 0.84 m/day to 4190 m/day, and a range of *logCa*  
355 from −8.1 to −4.4. The imposed range of injection rates correspond to  
356 flow rates at 0.02 to 70 m away from a typical injection well (with an  
357 injection rate of one million metric tonnes of scCO<sub>2</sub> per year over a  
358 screen length of 15 m assuming uniform flow) at a GCS site.

359 Despite complications that can arise from scCO<sub>2</sub>-induced wettability  
360 alteration such as those noted in the Introduction, we do not expect  
361 considerable wettability changes on micromodel surfaces subjected to  
362 repeated scCO<sub>2</sub> injection because of the relative short time of scCO<sub>2</sub>  
363 presence in the micromodel (aging time from minutes to hours), and  
364 the low ionic strength (0.01M NaCl) used in brine. Hu et al. (2017a,b)  
365 also reported constant contact angle measurements before and after  
366 repeated scCO<sub>2</sub> injection tests, using the same type of silica  
367 micromodel (differing only in pore geometry), similar experimental  
368 setup, and the same experimental pressure, temperature and brine  
369 salinity. Significant wettability changes from brine acidification after

370 scCO<sub>2</sub> dissolution may not be expected from (1) Hu et al. (2017a,b)  
371 mentioned above, and (2) Gribanova et al. (1976) who reported that as  
372 pH decrease from 6 to 3, contact angles only slightly increased from  
373 19° to 23° in the air–brine–silica system (Gribanova et al., 1976).  
374 Nevertheless, it should be recognized that solid surfaces in reservoirs  
375 are composed of diverse minerals, where non-uniform chemical  
376 interactions (both mineral dissolution and precipitation) and changes of  
377 electrochemical properties at brine-rock interface occur, inducing  
378 mixed-wet surfaces. These can be further enhanced by the non-  
379 uniform scCO<sub>2</sub> dissolution and mass transfer in brine, as previously  
380 reported (Chang et al., 2017, 2019a). Results from Wang et al. (2013)  
381 showed large contact angle variation on different pure mineral  
382 surfaces, and analysis suggested that the 38% differences in degrees  
383 of contact angle reported could manifest in 5–10% differences in  
384 capillary trapping or pressure. In this study, we further show the  
385 considerable changes of scCO<sub>2</sub> saturation after drainage by the mixed-  
386 wet solid surface.



**Figure 2.** Schematic of the experimental setup for scCO<sub>2</sub> injection and brine drainage tests.

## 2.4 Image analysis

Imaging was performed using an inverted microscope (Carl Zeiss, Observer Z1.m) equipped with a CCD camera (Carl Zeiss, Axiocam MRc5) that records images at the pore scale, and a Sony FDR-AX100 4K camcorder installed over the stage of the inverted microscope to record images at the pore-network scale. Segmentation and analysis of the images were conducted using ImageJ - public domain JAVA based software (Rasband, 1997-2019). Because efficient and direct

segmentation of  $\text{scCO}_2$  from brine and solid posts is difficult, the following steps were applied to the raw images: the raw images taken during a displacement test were first subtracted from the image taken at the initially water-saturated condition, followed by a median and a bilateral filtering (Chaudhury et al., 2011) of the resulting images. A threshold value was then unambiguously determined for each image to distinguish  $\text{scCO}_2$  phase from others. More details on the process and superimposed image comparing the contours before and after segmentation are presented in Figure S3 of the SI. We manually drew the contour of the  $\text{scCO}_2$  phase in the original subdomain ( $3.8 \times 3.7 \text{ mm}^2$ , as shown in Figure S3(a), also identical to Figure 5(d)) and calculated the pore space area occupied by  $\text{scCO}_2$ . By comparison with the segmented image in Figure S3(d), we showed errors  $< 1\%$ , which mostly originated from the edges and connectivities in the narrow pore throats. The resulting binary images were then used to present the displacement characteristics and calculate  $\text{scCO}_2$  saturation in the water-wet and two mixed-wet micromodels.

### 3. Results and discussion

In this section, we first present the contact angle measured for  $\text{scCO}_2$ -brine and mixed-wet patterns after coating treatment in Section 3.1, followed by  $\text{scCO}_2$  saturation and distribution at injection rates varying from  $\log Ca = -8.1$  to  $-4.4$  in the water-wet and two mixed-wet 2.5-D micromodels in Sections 3.2 and 3.3. In Section 3.4, we

421 further quantify the flow characteristics and topological scCO<sub>2</sub>  
422 distribution in different micromodels at the pore- and pore-network  
423 scale. In Section 3.5, the classic  $\log Ca - \log M$  diagram is presented and  
424 the impacts of pore geometry and mixed-wettability are discussed. We  
425 finally discuss the experimental implications on spatial variations of  
426 CO<sub>2</sub> saturation in a typical GCS site in Section 3.6.

### 427 **3.1 Contact angle and mixed-wet patterns after treatment**

428 The contact angle was measured for scCO<sub>2</sub>-brine at 8.5 MPa and  
429 45°C. Both of the untreated water-wet and treated mixed-wet  
430 micromodel were initially brine-saturated, followed by scCO<sub>2</sub> injection  
431 at a low rate until the scCO<sub>2</sub>-brine distribution in the micromodel was  
432 stable with time. The valves connecting to the inlet and outlet of the  
433 micromodel were then closed for 12 hours, and microscope images  
434 were taken at different locations of the pore network to measure  
435 scCO<sub>2</sub>-brine contact angles on solid posts. Menisci of scCO<sub>2</sub>-brine  
436 interface were selected such that each meniscus possessed a flat  
437 contact line of sufficient length so that the change in post geometry  
438 and surface roughness did not considerably affect the contact angle  
439 measurements. Figure 3(a) presents an example of the microscope  
440 image showing the variability of contact angle between scCO<sub>2</sub> (white)  
441 and brine (gray) in the treated micromodel (marked by the white  
442 dashed rectangle in Figure 3(d)). Within the local pore network domain  
443 of 2.6×1.9 mm<sup>2</sup>, the contact angle varies considerably, from 27° to



119°, indicating a mixed-wet system. This wide variation in contact angle is attributed to the non-uniform flow of coating solution during treatment. Bypassed patches filled by EG may retain originally water wet where coating is difficult to establish. Figure 3(b) further compares the contact angles obtained from over 60 menisci selected within the entire pore network. In the untreated micromodel, the values vary from 20° to 35°. With an average value of  $27^\circ \pm 4^\circ$ , the untreated micromodel shows a strong water-wet surface, similar to that reported by Hu et al. (2017b), who measured the average contact angle of scCO<sub>2</sub>-brine at 20° in a micromodel made of the same silica glass. It should be noted that their silica posts were fabricated with circular and smooth surfaces. The slightly higher contact angle measured in our micromodel may be attributed to the rough surface of the glass posts and associated contact line pinning. Figure 3(b) also shows considerable increases in the average contact angle and variations of contact angles after coating treatment. The contact angles after treatment vary from 34° to 145°, with an average value of  $89^\circ \pm 28^\circ$ . Note the menisci were selected over the entire pore network. This variation in contact angle indicates the spatial heterogeneity in wettability, ranging from strongly water-wet to strongly CO<sub>2</sub>-wet (Iglauer et al., 2015). This pore space heterogeneous wetting to brine results in different scCO<sub>2</sub> invasion characteristics, which are presented in detail in Section 3.3.

**Figure 3.** (a) A microscope image showing wide varieties of contact angles between scCO<sub>2</sub> (white) and brine (gray) within a local pore domain (indicated by the white dashed rectangle in (d)) after OTS treatment. (b) The contact angle measurements from over 60 selected menisci within the pore network for both untreated and treated micromodels. The quasi-steady state distribution of dyed EG (red color) in the micromodel after OTS injection at (c)  $\log Ca = -7.2$ , and (d)  $\log Ca = -3.9$ . OTS coating solution was injected from the left side of the micromodel as indicated by the blue arrow. The white arrow in (c) denotes the narrow intermediate-wet choke point established after OTS treatment.

Note that we measured the contact angle of menisci where both scCO<sub>2</sub> and brine were present. We assume the wettability of pore space invaded by coating solution during treatment is altered to non-wetting, and that saturated with EG retains its original water-wet surface characteristic. The assumptions were supported through measuring over 60 scCO<sub>2</sub>-brine menisci present within the pore space previously invaded by the coating solution or saturated by EG (see Figure 3b). We will provide more evidence and discussion by comparing the mixed-wettability patterns vs. CO<sub>2</sub> distribution in Section 3.4.

489 The distributions of dyed EG (red color) after treatment are shown  
490 in Figure 3(c) and 3(d), while the invaded coating solution and silica  
491 posts are presented non-fluorescent in blue to black color. The  
492 saturation of coating solution in the pore network is 0.50 and 0.70 at  
493 low (Figure 3(c)) and high (Figure 3(d)) injection rate, resulting in  
494 different areas that had wetting-altered pore surfaces. The average  
495 length and standard deviation of EG clusters after area-weighted in  
496 Figure 3(c) were measured as 2560  $\mu\text{m}$  and 1870  $\mu\text{m}$ , while the values  
497 are  $\sim 1/3$  at 870  $\mu\text{m}$  and 596  $\mu\text{m}$  in Figure 3(d). It should be noted that  
498 when the OTS solution advanced beyond the capillary barrier, it  
499 channeled through the relatively open pore domain outlined by the  
500 blue frame (Figures 1a. and 1c). By making the pore surfaces in this  
501 more open domain intermediate-wet, it became a location where  
502 invading  $\text{scCO}_2$  flow was focused after passing through the capillary  
503 barrier. Once through this location,  $\text{scCO}_2$  flow diverged as discussed  
504 later. Thus, this intermediate-wet region behaves as a choke point for  
505  $\text{scCO}_2$  invasion (see more details in Section 3.3).

506 The treated and untreated water-wet (WW) micromodels with  
507 identical geometry were then used in the  $\text{scCO}_2$  injection tests. For  
508 simplicity, we define (1) the capillary mixed-wet (CM) micromodel as  
509 the model was established at a low injection rate of coating solution  
510 (Figure 3(c)), where the intermediate-wet patches were capillary-force  
511 induced and heterogeneously distributed in the pore network; and (2)

the viscous mixed-wet (VM) micromodel as the model was established at a high injection rate of coating solution (Figure 3(d)), where the intermediate-wet patches were viscous-force induced and uniformly distributed in the pore network.

### **3.2 scCO<sub>2</sub> saturation and distribution in the 2.5-D water-wet (WW) micromodel**

Figure 4(a) shows the quasi-steady state scCO<sub>2</sub> distributions after displacement in the WW micromodel. The corresponding displacement rates ( $\log Ca$ ) and CO<sub>2</sub> saturations are presented in the parentheses. Depending on injection rates, the injected scCO<sub>2</sub> volumes at steady state range from 3 PVs at  $\log Ca = -8.1$  to 200 PVs at  $\log Ca = -4.4$ . The overall scCO<sub>2</sub> flow characteristics with varying displacement rates are distributed across the classic fingering regimes, i.e., capillary fingering dominates at low displacement rate ( $\log Ca < -6.4$ ), where scCO<sub>2</sub> flows in forward and lateral flow paths with large clusters of entrapped water; viscous fingering develops at large displacement rate ( $\log Ca > -6.1$ ), where scCO<sub>2</sub> widely invades the pore network and displaces water in the form of multiple narrow and well-connected flow paths. At intermediate rates ( $\log Ca = -6.4$  and  $-6.1$ ), crossover from capillary to viscous fingering is shown by the coexistence of distributed capillary fingering (near the upstream) and concentrated viscous fingering (near the downstream), similar to the experimental observations from Wang

et al. (2012), Ferer et al. (2004) and pore-network simulations by Lenormand et al. (1988).

Differing from above studies in a 2-D micromodel, however, we observe the great impacts of 2.5-D heterogeneity of pore geometry on  $\text{scCO}_2$  distribution. As shown in Figure 4(a) and for most cases ( $\log Ca < -5.1$ ),  $\text{scCO}_2$  invades the open slots (marked by the white circles) of the transverse barrier (see Figure 1(a)) that are close to the top and bottom boundaries, and bypasses the barrier and even some slots in center (marked by the red circles). The half-depth barrier hinders longitudinal  $\text{scCO}_2$  flow in the center and enhances transverse flow that bypasses the slots in front. We selected a local pore domain located by the red box in Figure 4(a) to better understand and discuss the  $\text{scCO}_2$  flow in Section 3.4.1. At  $\log Ca \geq -5.1$ ,  $\text{scCO}_2$  invades most of the slots under the strong viscous force. The capillary blockage of  $\text{scCO}_2$  and flow direction changes at a local pore domain are enhanced by the depth-reduced pore throat, comparing to that in a 2-D micromodel that possesses a constant pore throat depth.

### **3.3 $\text{scCO}_2$ saturation and distribution in the 2.5-D mixed-wet micromodels**

The fingering flow patterns and  $\text{CO}_2$  saturations in the two mixed-wet micromodels are presented in Figures 4(b) and 4(c). The classic flow regime transition from capillary fingering through crossover to viscous fingering can also be observed. At low injection rates ( $\log Ca =$

557  $-8.1$  and  $-7.4$ ),  $\text{CO}_2$  saturations are  $\sim 0.65$  and  $\sim 0.50$  in the VM and  
558 CM micromodel, but at the crossover zone ( $\log \text{Ca} = -6.4$ ), the values  
559 decrease to  $0.49$  and  $0.42$ . Further increasing the injection rates in both  
560 micromodels results in continuous increase of  $\text{CO}_2$  saturations to a  
561 similar value of  $0.80$  at maximum  $\log \text{Ca} = -4.4$ . The dependence of  $\text{CO}_2$   
562 saturation on solid surface wettability can be deduced from the 30  
563 displacement tests in the three micromodels. For instance, at low  
564 injection rates where the flow regime is dominated by capillary  
565 fingering ( $-8.1 \leq \log \text{Ca} < -6.4$ ),  $\text{CO}_2$  saturation in the VM micromodel  
566 is  $0.12$  to  $0.14$  higher than that in the WW micromodel (see Figures 4(a)  
567 and 4(c)), while the value in the CM micromodel is  $0.03$  lower at  $\log \text{Ca}$   
568  $= -8.1$ , and  $0.05$  to  $0.07$  higher at  $\log \text{Ca} = -7.1$  and  $-6.8$ . The  
569 saturation enhancement reaches maximum of  $0.18$  and  $0.12$  in the VM  
570 and CM micromodels at the intermediate-rate injections, where the flow  
571 regime is dominated by crossover from capillary to viscous fingering (  
572  $\log \text{Ca} = -6.4$  and  $-6.1$ ). At higher rates ( $\log \text{Ca} > -6.1$ ), the effect of  
573 wettability and pore geometry is suppressed by strong viscous force,  
574 resulting in high  $\text{CO}_2$  saturation in the three micromodels at the  
575 maximum injection rate. The overall higher  $\text{CO}_2$  saturation in the two  
576 mixed-wet micromodels at  $\log \text{Ca} \leq -6.1$  is attributed to the lower  
577 capillary entry pressure in pore networks having solid surfaces more  
578 wetting to the displacing  $\text{scCO}_2$ , similar to previous observations from  
579 Cottin et al. (2011), Zhao et al. (2016) and Hu et al. (2017a).

580 We show in Figure 4 that more CO<sub>2</sub> saturation enhancement occurs  
581 in the VM micromodel than that in the CM. In the two micromodels  
582 having identical pore geometry, the lower saturation enhancement in  
583 the CM micromodel can be attributed to effectively less area converted  
584 to hydrophobic surfaces relative to the VM micromodel. These  
585 converted hydrophobic surfaces, at the same time, are more  
586 heterogeneously distributed within the pore network (see Figure 2(a)  
587 and 2(b)), resulting in higher variations of capillary entry pressure  
588 among local pores/pore throats. The heterogeneously distributed  
589 hydrophobic surfaces then enhance channelized scCO<sub>2</sub> flow and hinder  
590 scCO<sub>2</sub> displacement efficiency. The non-uniform displacement and  
591 preferential CO<sub>2</sub> flow in micromodels and rock cores subject to pore-  
592 and sub-core scale heterogeneity has been extensively reported  
593 (Krevor, et al., 2011; Shi et al., 2011; Pini et al., 2012; Berg & Ott,  
594 2012; Berg et al., 2013; Chang et al., 2013, 2014; Chen et al., 2018). In  
595 a previous study, we presented in four centimeter-scale micromodels  
596 the change of CO<sub>2</sub> saturations by a factor of ~10 at similar imposed  
597 displacement rates, depending on the heterogeneity and anisotropy of  
598 pore networks (Chang et al., 2019b). We show here the importance of  
599 mixed wettability and its effect on displacement efficiency and CO<sub>2</sub>  
600 saturation, particularly at low displacement rates. In reservoirs where  
601 the flow rate is relatively slow ( $Ca < 10^{-7}$ ) and displacement is  
602 dominated by capillary fingering, CO<sub>2</sub> storage efficiency may be

collectively dependent on pore geometry, solid surface wettability and their heterogeneity.

Different CO<sub>2</sub> distributions in the two mixed-wet pore network are also shown in Figure 4. In the CM micromodel and at  $\log Ca < -4.4$ , the open slots invaded and bypassed by scCO<sub>2</sub> were spatially mixed (see the mixed white and red circles in Figure 4(b)), differing from that in the WW micromodel (see Figure 4(a)). More importantly, at intermediate-rate injections ( $-6.8 \leq \log Ca \leq -5.4$ ), we observed a single scCO<sub>2</sub> flow path developed at the barrier downstream (marked by the white arrows in Figure 4(b)). Lower and higher injection rates resulted in additional flow paths around it. This single flow path gradually developed into several dendritic paths towards the outlet. The unique scCO<sub>2</sub> flow pattern can be attributed to the preferential scCO<sub>2</sub> flow through the narrow intermediate-wet (instead of geometrically induced) choke point marked by the white arrow in Figure 2(a) and bounded by the blue rectangles in Figure 1(a) and 1(c). In the VM micromodel with more uniformly distributed intermediate-wet patches, scCO<sub>2</sub> broadly invaded the pore network with well-connected flow paths, except for a bypassed water body at the bottom left corner (see Figure 4(c) at  $\log Ca < -6.1$ ). No significant blockage from the transverse capillary barrier was observed, regardless of flow rate.

**Figure 4.** The quasi-steady state scCO<sub>2</sub> (shown in green) distribution after displacement in the micromodel of (a) water-wet (WW), (b)



capillary mixed-wet (CM) and (c) viscous mixed-wet (VM). The numbers in the parentheses are  $\log Ca$  values and  $CO_2$  saturations, respectively.  $scCO_2$  is injected at the left side of these images, as indicated by the blue arrow. The circles refer to the open slots in Figure 1c invaded (white) and bypassed (red) by  $scCO_2$ . The white arrows in (b) indicate the constrained  $scCO_2$  flow induced by the narrow intermediate-wet choke point. The red boxes in (a), (b) and (c) mark the local pore domains selected for analyzing pore-scale drainage characteristics and mixed-wettability effects in Figure 5 at  $\log Ca = -6.4$ .

In addition to the local choke point, we compare the mixed-wet patterns vs.  $scCO_2$  distribution in the entire pore network by overlapping Figure 4(b) at  $\log Ca = -8.1$ ,  $-6.1$  and  $-4.4$  with Figure 3(c), and Figure 4(c) at  $\log Ca = -8.1$ ,  $-6.1$  and  $-4.4$  with Figure 3(d). The resulting images (see more details in Figure S4 of the SI) show 70% of  $scCO_2$  in the CM pore network distributes within the intermediate-wet patches at  $\log Ca = -8.11$ , while the value in the VM pore network is 60%, indicating a more uniform  $CO_2$  distribution among the water-wet and intermediate-wet patches. Both values decrease with increasing injection rates to 50% at  $\log Ca = -4.4$ , when compact invasion dominates under strong viscous force regardless of heterogeneities in surface wettability and pore geometry. We do not expect or see exactly the same flow patterns even under the same

experimental conditions, as the randomness of pore size and grain surface, as well as the randomness of interfacial velocity at local pores/pore throats (Kataok et al., 1986). Most of the time we use (lumped) saturation, pressure data and statistics (e.g., the skeleton analysis here) to investigate the fundamental processes. We think we have sufficient reproducibility to distinguish the different flow regimes and mixed-wet impacts as shown by Figure S2 of the SI.

### **3.4 Quantifications on scCO<sub>2</sub> flow characteristics**

In this section, we quantify the scCO<sub>2</sub> flow characteristics that were descriptive in previous studies (e.g., Lenormand, et al., 1988; Zhang et al, 2011b; Wang et al., 2012), and discuss the effects of mixed-wettability at both pore and pore-network scales. The pore-scale analysis focuses on a local pore domain at  $3.8 \times 3.7 \text{ mm}^2$  in vicinity of the capillary barrier (indicated by the red squares in Figure 4). Quantification of the pore-network-scale flow characteristics was applied to all the displacement tests in the three micromodels.

#### *3.4.1 Pore-scale scCO<sub>2</sub> flow characteristics*

Figure 5(a) depicts the selected local pore domain composed of (1) ~100 solid posts (shown in black), (2) large pores 40  $\mu\text{m}$  deep (shown in yellow) and (3) tight pore throats 20  $\mu\text{m}$  deep (shown in red). The average pore and pore-throat size is measured as 204  $\mu\text{m}$  and 80  $\mu\text{m}$ , respectively from Figure 5(g). The porosity is 0.44, similar to the entire

671 pore network. Figure 5(d) represents the  $\text{scCO}_2$  flow paths (in white  
672 color) after displacement within the WW domain at  $\log Ca = -6.4$ . As  
673 shown in the figure,  $\text{scCO}_2$  invades the pore domain from the top left  
674 and the bottom right corner (see the red arrows), transversely flows  
675 through the domain along the red dotted arrows and flows out of the  
676 domain along the blue arrows. Note the bulk flow direction is from left  
677 to right. The blockage of  $\text{scCO}_2$  by the capillary barrier occurs, resulting  
678 in flow direction changes and bypass of tight (only 20  $\mu\text{m}$  deep) pore  
679 throats. After injection,  $\text{CO}_2$  saturation in the WW domain is stable at  
680 0.43. The OTS-altered intermediate-wet patches and  $\text{CO}_2$  distribution in  
681 the CM and VM domains are also compared for  $\log Ca = -6.4$ , and  
682 shown in white in Figures 5(b), 5(c), and Figures 5(e) and 5(f),  
683 respectively. The steady-state  $\text{CO}_2$  saturation after displacement is  
684 0.43 and 0.62, respectively in the CM and VM domain, among which  
685 90% and 64% distributes within the intermediate-wet patches.

686 The mixed-wettability changes the  $\text{scCO}_2$  saturation distribution vs.  
687 pore/pore throat size in Figure 5(h), which is obtained from aligning  
688 Figure 5(d), 5(e) and 5(f) with Figure 5(g). For all the three domains,  
689 the majority of  $\text{scCO}_2$  distributes in large pores/pore throats at 80 to  
690 400  $\mu\text{m}$ , with less than 1% in the tight pore throats ( $< 80 \mu\text{m}$  diameter  
691 and 20  $\mu\text{m}$  deep). The tight pore throats account for 3% of the pore  
692 space in the domain and the pore network. We also observe (1) similar  
693 correlations in the WW and CM domains, while a higher  $\text{CO}_2$  saturation

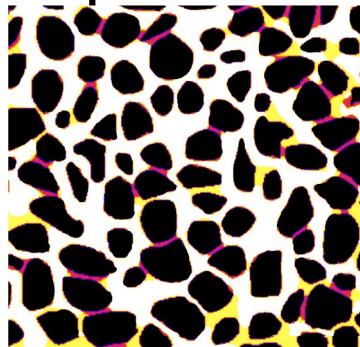
694 distribution occurs in smaller pores ( $< 200 \mu\text{m}$  diameter) in the VM  
695 domain (the accumulative  $\text{CO}_2$  saturation in these small pores is 0.29  
696 in the VM domain, while the value is 0.15 in the WW and CM); (2)  
697 larger saturation variations in large pores ( $>300 \mu\text{m}$ ) in the CM domain  
698 (note the more irregular red plot). These are consistent with Figure  
699 5(d), 5(e) and 5(f), and indicate different topologies of  $\text{scCO}_2$  flow path,  
700 i.e., better interconnections of flow in large and small pores/pore  
701 throats in the VM domain, and more constrained flow in the CM domain  
702 with bypass of small pore throats and even large pores.

703 Characterizing  $\text{scCO}_2$  distribution topology is important for  
704 understanding its invasion into pore networks and ultimately to help  
705 predict  $\text{scCO}_2$  plume shape in reservoirs. We apply a skeleton analysis  
706 in the same local pore domain using an Analyze Skeleton plugin in  
707 ImageJ to better quantify the topology of  $\text{scCO}_2$  flow paths and impacts  
708 of mixed-wettability. The skeleton geometry is defined as a thin  
709 version of that geometry which is equidistant to its boundaries. The  
710 binary images of  $\text{scCO}_2$  phase in the three types of pore domains  
711 (Figures 5 (d), (e), (f)) are first skeletonized in ImageJ and illustrated by  
712 branches and junctions shown in Figure 5(i), 5(j) and 5(k). A branch is  
713 composed of slab pixels that have exactly 2 neighbor pixels, while a  
714 junction is defined as the intersection of multiple (more than two)  
715 branches, i.e., the junction pixels have more than 2 neighbors. More  
716 details on the terminology and method are provided in Arganda-

717 Carreras et al. (2010). The numbers of branches and junctions, as well  
718 as the average branch length for scCO<sub>2</sub> flow paths were calculated and  
719 listed in Table 2. Also shown in Table 2 are values for the pore domain.  
720 The branch numbers increase from 61 in the CM to 135 in the WW, and  
721 reach maximum at 221 in the VM domain. Correspondingly, the  
722 junction number increases from 29 in the CM to 67 in the WW, and  
723 reaches maximum at 110 in the VM domain. Conversely, the average  
724 branch length is shortest in the VM and longest in the CM domain.  
725 These indicate a more interconnected flow topology of scCO<sub>2</sub> after  
726 displacement in the VM domain, and a more channelized scCO<sub>2</sub> flow in  
727 the CM domain. The average branch length of scCO<sub>2</sub> flow paths in the  
728 WW domain is 226 μm, which is close to the value of the pore domain  
729 (240), indicating a flow characteristic dominated by pore geometry.

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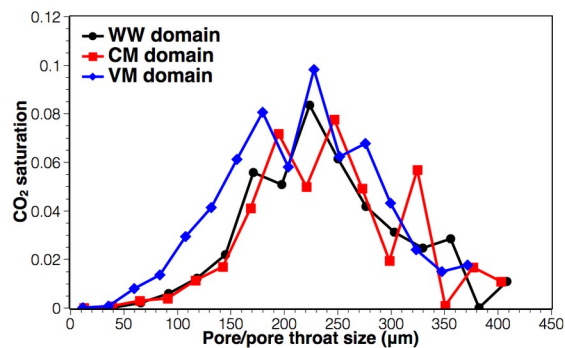
**Figure 5.** scCO<sub>2</sub> flow characteristics and mixed-wet effects through a topological skeleton analysis over a local pore domain (3.8 × 3.7 mm<sup>2</sup>).

(a) Pore characteristics of the originally WW domain, with full-depth (40 μm) pores shown in yellow and half-depth (20 μm) pore throats in red (these color indicators are also applied to (b), (c), (d), (e) and (f)). (b)

and (c) show the mixed-wet patterns in the CM and VM domains, with water-wet pore space shown in yellow and intermediate-wet pore space in white.

(d), (e) and (f) present the quasi-steady state scCO<sub>2</sub> (in white) distribution in the WW, CM and VM domains, respectively. The red dotted arrows indicate the scCO<sub>2</sub> flow directions within the domain,

along with red solid arrows for entrance and blue solid arrows for exit. (g) and (h) are the pore size distribution and CO<sub>2</sub> saturation distribution vs. pore/



pore throat size Skeletonized scCO<sub>2</sub> flow path within the pore domain quantified by the Local Thickness plugin in ImageJ software.

(i), (j) and (k) show the skeletonized CO<sub>2</sub> distribution composed by branches and

junctions in different pore domains.

Table 2. The branch and junction number, and average branch length for scCO<sub>2</sub> flow at  $\log Ca = -6.4$  and the selected pore domain by a skeleton analysis

Topological characteristics of scCO <sub>2</sub> flow paths			
Wetting type	Number of branches	Number of junctions	Average branch length (μm)
CM	61 (0.22)	29 (0.18)	389 (1.62)
WW	135 (0.48)	67 (0.42)	226 (0.94)
VM	221 (0.79)	110 (0.69)	194 (0.81)
Topological characteristics of pore domain			
	280	158	240

Note: The numbers in the parentheses are specific values calculated from ratios between scCO<sub>2</sub> flow paths and pore domain for Number of branches, Number of junctions and Average branch length.



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786 **Figure 6.** The specific branch and junction number, and specific  
787 branch length vs. *logCa* in the WW, CM and VM micromodel.

### 3.4.2 Pore-network-scale flow characteristics

We applied the topological analysis to the three micromodels to investigate scCO<sub>2</sub> flow characteristics at the pore-network scale. The branch and junction number, and the average branch length for scCO<sub>2</sub> flow paths ( $N_b, N_j$  and  $L$ ), and for the pore networks ( $N_{b,m}, N_{j,m}$  and  $L_m$ ) were first calculated, and their ratios, defined as specific branch number, specific junction number and specific branch length are presented as a function of  $\log Ca$  in Figure 6. In the WW micromodel, the branch and junction numbers that keep relatively high plateau values at  $\log Ca < -6.5$  (black lines Figure 6(a) and 6(b)) correspond to the wide invasion and randomly distributed forward and lateral flow paths observed in the capillary fingering regime. The considerable reduction in branch and junction numbers at  $\log Ca = -6.4$  and  $-6.1$  is consistent with the crossover from capillary to viscous fingering and decreased displacement efficiency. At higher injection rates ( $\log Ca > -6.1$ ) where viscous fingering dominates the flow regime, the branch and junction numbers increase with new developed and interconnected flow paths. The variation of the specific branch length as a function of  $\log Ca$  (Figure 6(c)) is generally mirrored to specific branch and junction number vs.  $\log Ca$ . This is expected as flow paths develop interconnected, the branch and junction number increase whereas the average branch length decreases.

Figure 6 also presents the largest branch and junction numbers in the VM micromodel among the three. This is in favor of GCS by increasing displacement efficiency. The CM micromodel yields longest branch length and lowest branch and junction number. In mixed-wet caprocks, the channelized flow developed within the intermediate-wet patches may increase capillary leakage of scCO<sub>2</sub> accumulation below because of the locally reduced capillary entry pressure.

### 3.5 CO<sub>2</sub> saturation vs. capillary number considering mixed wettability

Figure 7(a) presents the relations between CO<sub>2</sub> saturation and  $\log Ca$  for the displacement experiments conducted in the three wetting types of micromodels. An alternative definition of capillary number ( $Ca^i$ ) from Lenormand et al. (1988) that considers the solid surface wettability is calculated as follows:

$$Ca^i = (\mu \times \bar{u}) / (\sigma \times \cos\theta), \quad \text{Eq. (2)}$$

Where  $\cos\theta$  is derived from the pore space area ( $A$ ) and average contact angle of the water-wet and intermediate-wet patches:

$$\cos\theta = \frac{A_1 \cos\theta_1 + A_2 \cos\theta_2}{A_1 + A_2} \quad \text{Eq. (3)}$$

For the CM micromodel,  $\theta_1 = 27^\circ$ ,  $A_1/(A_1 + A_2) = 0.50$ ;  $\theta_2 = 89^\circ$ ,  $A_2/(A_1 + A_2) = 0.50$ ; for the VM micromodel,  $\theta_1 = 27^\circ$ ,  $A_1/(A_1 + A_2) = 0.30$ ;  $\theta_2 = 89^\circ$ ,  $A_2/(A_1 + A_2) = 0.70$ . For the original WW micromodel,  $\theta_1 = \theta_2 = 27^\circ$ . The

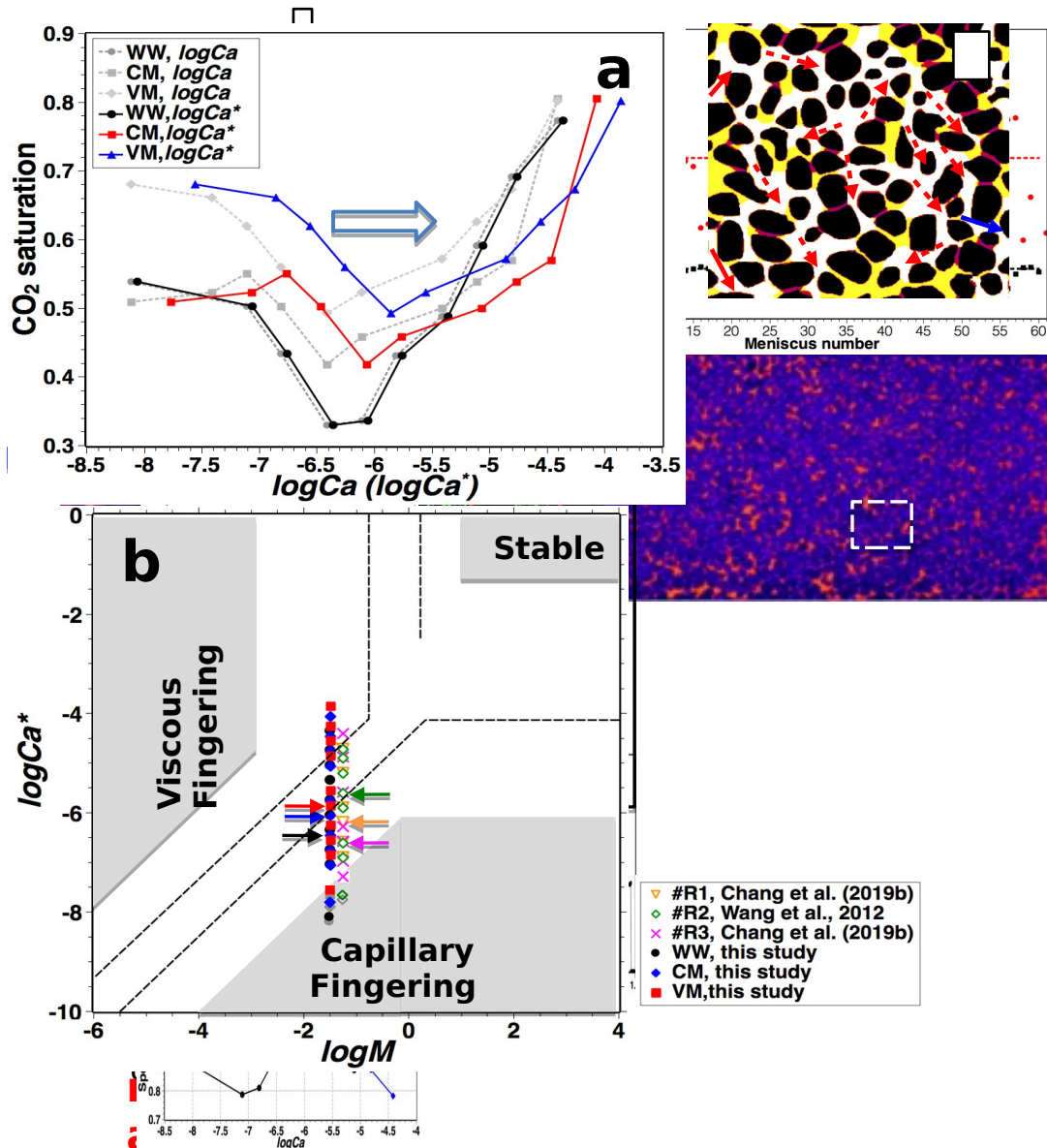
831 CO<sub>2</sub> saturation vs.  $\log Ca^i$  relations for the three micromodels are  
832 shown by colored plots in Figure 7(a), which translate rightward from  
833 the CO<sub>2</sub> saturation -  $\log Ca$  relations at 0.4 unit in the CM and 0.6 unit  
834 in the VM micromodel. In the WW micromodel, the two plots overlap  
835 without considerable change due to the small contact angle. These  
836 correspond to the fact that the presence of intermediate-wet rock  
837 surfaces (larger contact angles) further assures viscous fingering  
838 within the near-field network and transition to the capillary fingering  
839 regime occurs closer to the injection well. The  $Ca^i$  that consider solid  
840 surface wettability may be able to better quantify the fingering and  
841 crossover flow regimes. However, caution is needed as variations of  
842 contact angles and their spatially heterogeneous distributions are  
843 likely to be more complex in natural reservoirs formations than in the  
844 two treated micromodels.

845 Figure 7(b) illustrates the classic  $\log Ca^i$ -  $\log M$  diagram, with  
846 boundaries of different displacement patterns from Lenormand et al.  
847 (1988) shown in gray and Zhang et al. (2011) in dash lines. The  
848 different boundaries observed from the two studies were attributed to  
849 the different pore geometries and pore-size variations. The values of  
850  $\log Ca^i$  and  $\log M$  used in this study are shown by solid symbols. In a  
851 previous study (Chang et al., 2019b), we conducted scCO<sub>2</sub>  
852 displacement experiments at 40 °C and 9 MPa in (1) an anisotropic  
853 and homogeneous micromodel consisting of elliptical silicon posts, with

854 estimated transverse-to-longitudinal permeability ratio of 0.63; (2) a  
855 heterogeneous sandstone-analogue micromodel, which was patterned  
856 based on section micrographs of a Mt. Simon sandstone core extracted  
857 from the injection well of the Illinois Basin - Decatur project (Senel et  
858 al., 2014). We include data on the two micromodels (hollow symbols)  
859 and refer them as #R1 and #R3 in the figure. Under similar conditions  
860 at 41°C and 9.0 MPa, Wang et al. (2012) conducted scCO<sub>2</sub>  
861 displacement tests in a homogeneous isotropic pore network that  
862 consisted of 200 µm cylindrical silicon posts, 120 µm pore bodies and  
863 26.7 µm pore throats. Their results were shown and referred as #R2 in  
864 Figure 7(b) (see more detailed images on the referred micromodels in  
865 Figure S5 of the SI). All the referred data were obtained in micromodels  
866 with water-wet solid surfaces ( $\theta=15^\circ$ ) and similar pore/pore throat  
867 depth (35 to 37 µm). We tried to include as much data as possible for  
868 better comparison, however, were hindered by the narrow capillary  
869 number range applied in previous studies, particularly by the  
870 deficiency at low rates ( $\log Ca^i < -7.0$ ) that are dominant at GCS sites.

871 The colored arrows in Figure 7(b) indicate the flow regime crossover  
872 with minimum CO<sub>2</sub> saturation observed in each study. The crossover  
873  $\log Ca$  values in this and referred studies, regardless of pore  
874 geometries or surface wettabilities, ranges from -5.6 to -6.6,  
875 generally lower than the boundaries (-4.6 to -5.8) predicted by Zhang  
876 et al. (2011) at a similar  $\log M$  value of -1.34. The displacing fluid

(dodecane) viscosity from Zhang et al. (2011), however, is almost two orders of magnitude higher at 1.35 mPa·s than that of scCO<sub>2</sub> used in this study, while the interfacial tension (IFT) between the displacing and resident fluid (polyethylene glycol 200) is lower at 13.87 mN/m. The low scCO<sub>2</sub> viscosity and high IFT with brine may intensify interfacial instability for scCO<sub>2</sub>-brine displacement and result in lower  $\log Ca^c$  values for flow regime changes from capillary fingering to crossover. In a 2-D homogeneous micromodel, Armstrong & Berg (2013) showed that individual pore drainage events occurred at an intrinsic rate, which was independent of bulk flow rate. Further modeling results indicated the two-phase interfacial velocity increased with decreasing viscosity of the displacing phase or increasing interfacial tension and for the same capillary number, the velocity of two-phase interface can differ by an order of magnitude or more (Armstrong et al., 2015). The broad distribution in  $Ca$  associated with crossover (minimum nonwetting phase saturation indicated by arrows in Figure 7(b)) suggests that capillary number alone does not explain the pore-scale displacement. While most studies focus on the fingering flow regimes and transitions using fluid pairs of different viscosity ratios (Dong et al., 2011; Zhang et al., 2011a,b; Dehoff et al., 2012; Wang et al., 2012; Liu et al., 2013; Zheng et al., 2017), additional studies are required using fluid pairs of same viscosity ratio but different in displacing fluid viscosities or IFTs.



**Figure 7.** (a) The correlations of CO<sub>2</sub> saturation vs.  $\log Ca$  (the gray dash lines) and CO<sub>2</sub> saturation vs.  $\log Ca^*$  (the colored solid lines) for the displacement experiments conducted in the three wetting

types of micromodels. The blue arrow indicates the shift direction of  $\log Ca^i$  from  $\log Ca$ . (b)  $\log Ca^i - \log M$  stability diagram showing three stability areas and the locations of the displacement experiments in this and previous studies for scCO<sub>2</sub> and water. The dash lines are the stability boundaries from Zhang et al. (2011b) and the gray zones denote the stability areas from Lenormand et al. (1988). The colored arrows mark the conditions at saturation minimum in each study.

### 3.6 Field implications

The 30 tests under the wide range of displacement rates allowed investigations on the full spectrum of fingering flow regimes, CO<sub>2</sub> saturations, and mixed-wettability impacts. These results have implications for a GCS site. In Figure 8, we show CO<sub>2</sub> saturation vs. distance to the injection well calculated from the typical CO<sub>2</sub> flow velocity in a GCS site. We assume (1) at the field, CO<sub>2</sub> is injected at a volumetric rate ( $Q$ ) of 10,000 m<sup>3</sup>/d over a screen length of 15 m, and (2) scCO<sub>2</sub> density ( $\rho$ ) from reservoir pressure and temperature is close to that at experimental conditions and CO<sub>2</sub> velocities in the formation is radially uniform. This volumetric rate corresponds to an annual injection of one million metric tonnes of CO<sub>2</sub> at 8.5 MPa and 45 °C (this study), and 1.8 million metric tones of CO<sub>2</sub> at 9 MPa and 40 °C (Wang et al., 2012; Chang et al., 2019b). The distance from the injection well can then be calculated as follows:



$$d = \frac{Q}{2\pi h \bar{u}} \quad \text{Eq. (4)}$$

Where  $d$  refers to the (radial) distance to the injection well,  $h$  is the screen length of the injection well, and  $\bar{u}$  is the CO<sub>2</sub> velocity that equals to the lab values listed in Table 1.

Results from Wang et al. (2012) and Chang et al. (2019b) in Micromodel #R1, #R2, #R3 and #R4 were also included in Figure 8, with estimated CO<sub>2</sub> saturations from their published figures. #R4 refers to an anisotropic and homogeneous micromodel that consists of elliptical silicon posts with estimated transverse-to-longitudinal permeability ratio of 6.86 (see Figure S5 for more details in the SI). #R4 also possesses water-wet solid surface ( $\theta=15^\circ$ ) and constant pore/pore throat depth at 37  $\mu\text{m}$ . CO<sub>2</sub> saturations after displacement in this micromodel showed high values ( $\sim 0.90$ ) over the applied injection rates, with no crossover flow observed.

In the three micromodels of identical geometry, CO<sub>2</sub> saturation varies as a function of distance to the injection well, depending on the wettability. Comparing to the WW micromodel, VM enhances CO<sub>2</sub> saturation over the investigated distance up to 130 m away from the injection well, while CM only enhances the value at locations 0.25 to 25 m away. In the WW and two mixed-wet micromodels, the crossover from viscous to capillary fingering occurs at locations close to the injection well (1.27 to 2.50 m), and the two mixed-wet systems

967 accelerate the saturation rebound to saturation plateau. For the seven  
968 micromodels investigated, viscous fingering flow dominates the  
969 constrained locations  $< 1$  m away from the injection well, imposing a  
970 very limited impact on the storage efficiency at the field. This again  
971 indicates that laboratory experiments at low injection rates are  
972 important for obtaining more field-relevant implications.

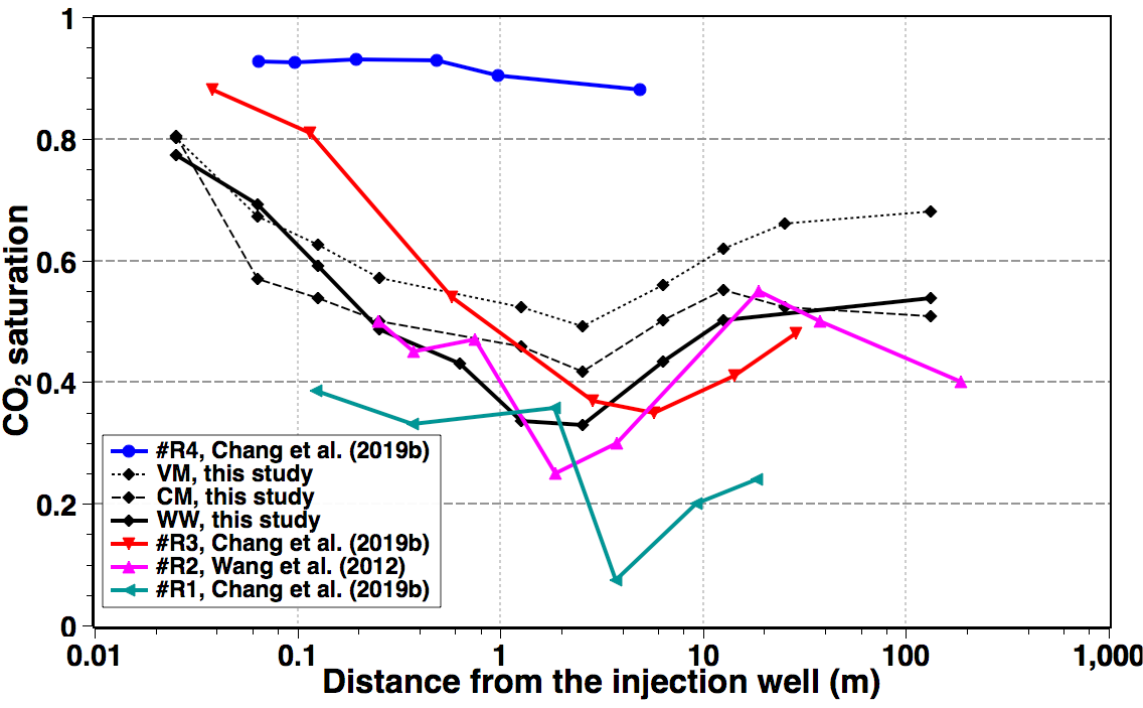
973 Figure 8 also indicates the great impact of pore-network anisotropy  
974 and heterogeneity on CO<sub>2</sub> saturation. As shown in the figure, pore-  
975 network anisotropy imposes the most pronounced effect on CO<sub>2</sub>  
976 saturation. The anisotropic Micromodel #R4 with high transverse-to-  
977 longitudinal permeability ratio (6.86:1) results in highest CO<sub>2</sub>  
978 saturations, while the anisotropic Micromodel #R1 with low transverse-  
979 to-longitudinal permeability ratio (0.63:1) yields lowest CO<sub>2</sub> saturations  
980 at 0.10 to 0.40. The pore size surprisingly does not have a considerable  
981 impact on CO<sub>2</sub> saturation at locations  $> 20$  m away from the injection  
982 well, when comparing Micromodel #R2 with Micromodel #R3 and the  
983 2.5-D heterogeneous WW micromodel in this study. A higher CO<sub>2</sub>  
984 saturation was expected in Micromodel #R2 containing large 120  $\mu\text{m}$   
985 pore and in the WW micromodel with an average pore size of 190  $\mu\text{m}$ .  
986 The average pore size of Micromodel #R3 is smaller at 33  $\mu\text{m}$ . Note the  
987 small pore depth relative to pore size in #R2 and the WW micromodel,  
988 which may limit the displacement efficiency since (1) Wang et al.  
989 (2012) observed the transition of scCO<sub>2</sub> flow from widely distributed

990 forward and lateral flow paths to one gradually narrowing finger  
991 leading to the outlet and bypass the major pore domain by the small  
992 variations of pore depth in Micromodel #R2, and (2) we observed the  
993 preferential flow of CO<sub>2</sub> through the deep open slots in the transverse  
994 capillary barrier and bypass the majority of pore domain downstream  
995 in the WW micromodel. The effect of depth variation is weakened in  
996 Micromodel #R3 due to the similar pore size and depth. We emphasis  
997 here the importance of pore/pore throat depth in determining two-  
998 phase flow and saturation, and suggest careful consideration of the  
999 third dimension during micromodel design and fabrication.

1000       It is noted that results from this and previous studies were obtained  
1001 in centimeter-scale micromodels that possess pore size variations in a  
1002 range of tens to hundreds of micrometers. Great caution is needed in  
1003 using these laboratory results for understanding field-scale GCS  
1004 behavior (e.g., predicting the CO<sub>2</sub> saturation vs. distance to the  
1005 injection well using Figure 8) because heterogeneities and gravity are  
1006 important at the larger scale. In the field, the viscous/capillary scCO<sub>2</sub>  
1007 fingers may coincide with high-permeability channels developed at the  
1008 meter to kilometer scale, while local pore structures and small fingers  
1009 may become secondary in affecting the scCO<sub>2</sub> plume (Birkholzer et al.,  
1010 2015). In addition, gravity could not be considered in these laboratory  
1011 experiments on horizontal pore networks. The interplay between  
1012 viscous/capillary fingering and gravity are also important as gravity is

1013 dominant in shaping 3-D plumes and increasing leakage potential  
1014 through the caprock (Zhou & Birkholzer, 2011; Trevisan et al., 2017).

1015 **Figure 8.** CO<sub>2</sub> saturation vs. distance from the injection well (in  
1016 logarithmic scale) for the displacement experiments conducted in the  
1017 three micromodels and in Wang et al. (2012) and Chang et al. (2019b)



1018 using different pore networks under similar experimental conditions.

1019

## 1020 4. Conclusions

1021 Secure and efficient CO<sub>2</sub> storage in a geological formation can be  
1022 affected by the mixed-wettability of reservoir rocks, and therefore this  
1023 characteristic requires a systematic investigation. By applying a

1024 coating solution to modify wettability in a 2.5-D micromodel, we  
1025 created two mixed-wet systems, one viscous force-induced resulting in  
1026 uniformly distributed intermediate-wet patches; and one capillary  
1027 force-induced resulting in heterogeneously distributed intermediate-  
1028 wet patches. The two mixed-wet and the originally water-wet  
1029 micromodels were then compared in scCO<sub>2</sub> injection experiments. A  
1030 full spectrum of flow-regime transition from capillary fingering through  
1031 crossover to viscous fingering was observed in the three micromodels.  
1032 The pronounced effects of 2.5-D heterogeneity of pore network on  
1033 scCO<sub>2</sub> distribution and saturation were indicated by (1) scCO<sub>2</sub>  
1034 preferential flow along the large 40 µm deep pores and bypass of tight  
1035 20 µm deep pore throats, and (2) the comparisons between  
1036 micromodels with varying pore characteristics. A detailed analysis on  
1037 CO<sub>2</sub> saturation and topological distribution showed (1) high storage  
1038 efficiency and wide interconnections of CO<sub>2</sub> flow paths in reservoirs  
1039 containing more and uniformly distributed intermediate-wet and water-  
1040 wet patches, and (2) hindered storage efficiency and channelized CO<sub>2</sub>  
1041 flow paths in reservoirs containing heterogeneously distributed  
1042 intermediate-wet patches. The channelized flow of scCO<sub>2</sub> (especially at  
1043 locations close to injection well) may increase leakage potential  
1044 through caprock. This pore-network-scale study indicates the  
1045 importance of mixed-wettability in determining CO<sub>2</sub> storage efficiency

and spatial variation in depleted hydrocarbon reservoirs and others  
that may present mixed-wet rock surface.

## **Supporting Information (SI)**

More detailed information on the contact angle measurements,  
characterizations on the drainage flow regimes and referred  
micromodels are provided in the SI.

## **Conflicts of interest**

The authors declare no competing financial interest.

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[https://datadryad.org/stash/share/  
MMmArpl0nxlOdS2jO4VF0dFWi9NLFHFB2HzoYx9EGSc](https://datadryad.org/stash/share/MMmArpl0nxlOdS2jO4VF0dFWi9NLFHFB2HzoYx9EGSc).

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